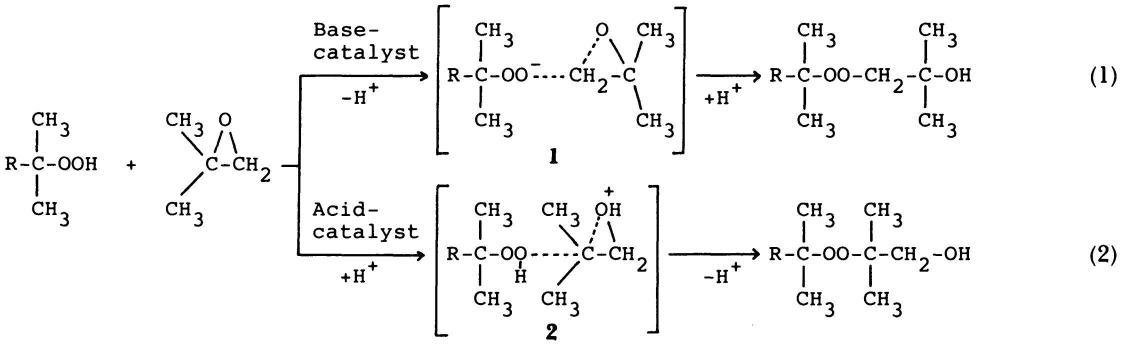
A Convenient Synthesis of 2-*t*-Alkyldioxy-2-methyl-1-propanols

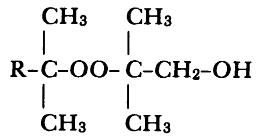
Yoshiki Higuchi,* Kazuo Matsuyama, and Takeshi Komai
Chemical & Explosives Research Laboratory, Nippon Oil & Fats Co., Ltd.,
Taketoyo-cho, Chita-gun, Aichi-ken 470-23

(Received October 5, 1987)

Synopsis. Several 2-*t*-alkyldioxy-2-methyl-1-propanols have been synthesized conveniently by a ring-opening reaction of 1,2-epoxy-2-methylpropane with *t*-alkyl hydroperoxides in the presence of halogenated acetic acid catalysts.

Hydroxy-substituted dialkyl peroxides and their derivatives have been of interest as a radical source at high temperatures.[1] Some of them have been prepared by the reaction of epoxides with *t*-alkyl hydroperoxides.[2–5] This reaction proceeds via different paths, depending on the type of catalyst. When 1,1-dimethylethyl hydroperoxide was reacted with 1,2-epoxy-2-methylpropane, for instance, *t*-alkyl *n*-alkyl peroxide; 2-(1,1-dimethylethyldioxy)-1,1-dimethylethanol, was obtained in the presence of such base-catalysts as potassium hydroxide[2] and aluminium oxide.[3] On the other hand, *t*-alkyl *t*-alkyl peroxide; 2-(1,1-dimethylethyldioxy)-2-methyl-1-propanol, was formed in the presence of an acid catalyst such as sulfuric acid.[5] This result may be explained by the difference in the stabilization at the transition states (**1** and **2**) involved with the two types of the catalysts, as is shown above. Although several studies have been reported on base-catalyzed reactions, there seems to have been only one report concerning an acid-catalyzed reaction, and its yield was very low (20% yield). Therefore, we studied acid-catalyzed reactions in an attempt to prepare *t*-alkyl *t*-alkyl peroxides **3** in good yields, such peroxides are suitable as radical sources at high temperatures and are not liable to undergo a radical-induced decomposition.[1c]





3

$$R\text{-}C(CH_3)_2\text{-}OO\text{-}C(CH_3)_2\text{-}CH_2\text{-}OH$$

3; **a**: R=CH_3
b: R=CH_3CH_2
c: R=$CH_3CH_2CH_2$
d: R=$(CH_3)_3CCH_2$

Results and Discussion

The synthesis of **3a** was carried out by adding 1,2-epoxy-2-methylpropane, drop by drop, to a mixture of 1,1-dimethylethyl hydroperoxide, an acid catalyst and solvent; then the mixture was stirred for 30 min at 35 °C. The yield of **3a** was determined by GC analysis with an internal standard; it is shown in Table 1. The results indicate that the yield depends significantly on the types of acid catalysts and solvents. When dichloro-, trichloro-, and trifluoroacetic acids were used as acid catalysts, **3a** was obtained in a 40—70% yield within 30 min. This reaction is influenced by the amount of the catalyst. The yield of **3a** was only 6% in the presence of trifluoroacetic acid (0.01 mol equivalent) and did not increase even though the reaction mixture was stirred more than 20 h continuously. Similarly, when *p*-toluenesulfonic acid, amberlyst, and such weak acid-catalysts as 30% sulfuric acid and chloroacetic acid were used, the yield was below 23%. The decomposition of the hydroperoxide was observed throughout the reaction in the presence of such strong acid catalysts as sulfuric acid (more than 50%), trifluoromethanesulfonic acid, chlorosulfuric acid, and aluminium chloride. The yield was higher in such nonpolar solvents as hexane, chloroform, carbon tetrachloride, benzene, and nitrobenzene than in the polar solvents. When 1,1-dimethylethyl hydroperoxide was reacted with a reaction mixture containing 2-hydroxy-2-methylpropyl trifluoroacetate,[6] which was formed by the reaction of 1,2-epoxy-2-methylpropane with trifluoroacetic acid in equivalent weights for 30 min at 35 °C, the formation of **3a** was only a trace on GC. These findings indicate that the reaction does not proceed via the addition-elimination of the acid catalyst, but via the nucleophilic attack of 1,1-dimethylethyl hydroperoxide on a protonated epoxide intermediate, such as in the normal acid-catalyzed ring-opening reactions.[7]

Three other 2-*t*-alkyldioxy-2-methyl-1-propanols were synthesized under optimum reaction conditions

Table 1. Influence of Various Acid Catalysts and Solvents on the Yield of **3a**[a]

Acid-catalyst	Mol/mol of 1,2-epoxy-2-methylpropane	Solvent	Yield of **3a**[b] %
Trifluoroacetic acid	1.0	Benzene	54
Trifluoroacetic acid	0.5	Benzene	69
Trifluoroacetic acid	0.1	Benzene	43
Trifluoroacetic acid	0.01	Benzene	6
Trichloroacetic acid	0.5	Benzene	65
Dichloroacetic acid	0.5	Benzene	59
Chloroacetic acid	0.5	Benzene	23
p-Toluenesulfonic acid	0.5	Benzene	20
Amberlyst 15[c]	0.5	Benzene	12
30% H_2SO_4	0.5	Benzene	18
Trifluoroacetic acid	0.5	Hexane	69
Trifluoroacetic acid	0.5	Chloroform	66
Trifluoroacetic acid	0.5	Carbon tetrachloride	66
Trifluoroacetic acid	0.5	1,4-Dioxane	41
Trifluoroacetic acid	0.5	Diethyl ether	52
Trifluoroacetic acid	0.5	Acetonitrile	44
Trifluoroacetic acid	0.5	Nitrobenzene	59
Trifluoroacetic acid	0.5	Isopropyl alcohol	52
Trifluoroacetic acid	0.5	Methanol	31
Trifluoroacetic acid	0.5	*N,N*-Dimethylformamide	14

a) 1,2-Epoxy-2-methylpropane of 1.44 g (0.020 mol) was used. b) Based on 1,2-epoxy-2-methylpropane. c) Commercial product from Rohm and Haas company.

Table 2. Synthesis of 2-*t*-Alkyldioxy-2-methyl-1-propanols[b]

Product	Yield[c] %	Bp (°C/mmHg[a])	IR (neat)/cm^{-1}
3a	69	52—53/6[d]	875 (ν_{O-O}), 3450 (ν_{O-H})
3b	72	46—47/3	875 (ν_{O-O}), 3450 (ν_{O-H})
3c	70	57—58/4	875 (ν_{O-O}), 3450 (ν_{O-H})
3d	62	46—48/0.5	875 (ν_{O-O}), 3450 (ν_{O-H})

Product	^{1}H NMR (δ/ppm) [$CDCl_3$/TMS]	MS (m/z)	n_D^{20}	Anal. (%) Found (Calcd)
3a	1.21 [s, 6H, $-(CH_3)_2C-$], 1.26 [s, 9H, $(CH_3)_3C-$], 2.35 [s, 1H, -OH], 3.59 [s, 2H, $-C\underline{H}_2-OH$]	162 (M^+)	1.4184	C: 58.78 (59.23), H: 10.99 (11.18)
3b	0.89 [t, J=7.5Hz, 3H, $C\underline{H}_3CH_2-$], 1.21 [s, 6H, $-(CH_3)_2C-$]×2, 1.60 [q, J=7.5Hz, 2H, $CH_3C\underline{H}_2-$], 2.33 [s, 1H, -OH], 3.60 [s, 2H, $-C\underline{H}_2-OH$]	176 (M^+)	1.4251	C: 60.94 (61.33), H: 11.52 (11.44)
3c	0.92 [t, J=7.5Hz, 3H, $C\underline{H}_3CH_2-$], 1.19 [s, 6H, $-(CH_3)_2C-$], 1.21 [s, 6H, $-(CH_3)_2C-$], 1.5 [m, 4H, $-(CH_2)_2-$], 2.30 [s, 1H, -OH], 3.60 [s, 2H, $-C\underline{H}_2-OH$]	190 (M^+)	1.4279	C: 62.60 (63.12), H: 11.63 (11.65)
3d	1.02 [s, 9H, $(C\underline{H}_3)_3CCH_2-$], 1.20 [s, 6H, $-(CH_3)_2C-$], 1.33 [s, 6H, $-(CH_3)_2C-$], 1.57 [s, 2H, $-CH_2-$], 2.33 [s, 1H, -OH], 3.60 [s, 2H, $-C\underline{H}_2-OH$]	218 (M^+)	1.4371	C: 65.62 (66.01), H: 12.10 (12.00)

a) 1 mmHg=133.322 Pa. b) 1,2-Epoxy-2-methylpropane of 18.7 g (0.26 mol) was used. c) Based on 1,2-epoxy-2-methylpropane. d) Lit,[5] 38—40 °C/3 mmHg.

of **3a**; the results are listed in Table 2. The peroxides were obtained in 62—72% yields. The crude products were purified by washing with water and an aqueous solution of sodium hydroxide to remove any unreacted materials and by-products and by then distilling them under vacuum pressures. The structures of **3a—d** were identified by means of their boiling points, their refractive indices, and the elemental-analysis, IR, NMR, and mass spectral data, as are shown in Table 2.

Experimental

The reaction products were analyzed by means of gas chromatography (GC) on a Shimadzu Model GC-2D chromatograph using a 1.4 m×2.6 mm glass column of 5% Silicone GE SE-30 on 60—80 mesh Uniport HP, with undecane and dodecane as internal standards. The ^{1}H NMR spectra were obtained, using chloroform-*d* as the solvent, on a JEOL Model JNM-MN-100 spectrometer. The IR spectra were recorded on a JASCO Model A-3 spectrometer.

Purification of Hydroperoxides. The corresponding hydroperoxides of **3a** and **3b** were purified by distillation. The commercial products obtained from the Nippon Oil & Fats Co., Ltd., for the corresponding hydroperoxides of **3c** and **3d** were purified by the isolation of the sodium salts, the regeneration of the hydroperoxides by carbon dioxide, and distillation.

Synthesis of Dialkyl Peroxides. A typical synthesis of **3a** was carried out as follows. 1,2-Epoxy-2-methylpropane (18.7 g, 0.26 mol) was added slowly to a solution of trifluoroacetic acid (14.8 g, 0.13 mol), 1,1-dimethylethyl hydroperoxide (46.5 g, 0.52 mol), and benzene 25 cm^3 below 10 °C, after which the reaction mixure was stirred at 35 °C for 30 min. The yield of **3a** was determined by GC, using undecane as an internal standard; it is shown in Table 2. The reaction mixture was washed with water, an aqueous solution of 5% NaOH, and a saturated solution of NaCl, and then dried over anhydrous $MgSO_4$. After the solvent had been removed, the residue (36.7 g) was distilled to give **3a** (22.4 g). The purity, as checked by GC, was 96.5%.

The syntheses of **3b—d** were carried out by using the corresponding hydroperoxides in place of 1,1-dimethylethyl hydroperoxide by a method similar to that used for **3a**. Crude products were purified by distillation after the residual hydroperoxides in the reaction mixture had been changed into the corresponding alcohols by the use of an aqueous solution of Na_2SO_3. The purities, as checked by GC, were more than 95%.

References

1) N. G. Gayload, Ger. Offen., 2440951 (1975); *Chem. Abstr.*, **83**, 11196h (1975); H. C. Stevens, U. S. Patent, 3640985 (1972); *Chem. Abstr.*, **76**, 142469q (1972); O. L. Mageli and W. A. Swarts, Ger. Offen., 2631911 (1977); *Chem. Abstr.*, **86**, 156821e (1977); A. A. Syrov, S. S. Ivanchev, O. N. Primachenko, V. A. Demidova, B. V. Polosov, I. V. Fionov, and E. N. Barentsevich, Ger. Offen., 2945151 (1980); *Chem. Abstr.*, **93**, 113983m (1980); R. Hiatt, "Organic Peroxides," Vol. III, ed. by D. Swern, John Wiley & Sons, New York (1972), Chap. 1.

2) M. R. Barusch and J. Q. Payne, *J. Am. Chem. Soc.*, **75**, 1987 (1953).

3) H. Kropf, H. M. Amirabadi, M. Mösebach, A. Torkler, and H. von Wallis, *Synthesis*, **1983**, 587.

4) H. Kropf, M. Ball, H. Schroder, and G. Wite, *Tetrahedron*, **30**, 2943 (1974).

5) W. H. Richardson and R. S. Smith, *J. Org. Chem.*, **33**, 3882 (1968).

6) In a separate experiment, 2-hydroxy-2-methylpropyl trifluoroacetate was isolated and confirmed by its IR spectra.

7) K. Ichikawa and M. Inoue, *Yuki Gosei Kagaku Kyokai Shi*, **38**, 61 (1980); R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 797 (1959); F. A. Long and J. G. Pritchard, *J. Am. Chem. Soc.*, **78**, 2663 (1956).